

COMPARATIVE STUDY OF As, Cr AND Cu ACCUMULATION BY MAIZE (*Zea Mays* L) AND OKRA (*Abelmoschus esculentus*) PLANTS IN CCA CONTAMINATED SOIL.

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ABSTRACT : Pot experiments were carried out to examine the phytoextraction capacity of maize and okra plants for As, Cr and Cu from poultry manure amended chromated-copper-arsenate (CCA) contaminated soil. The physico-chemical properties of the soil: pH 6.20 ± 0.040 ; organic matter content $2.15 \pm 0.40\%$; cation exchange capacity $47.86 \pm 0.62\text{meq}/100\text{g}$; clay 25%, silt 2% and sand 73% and pseudototal levels of As, Cr and Cu of $32.09 \pm 2.48\text{mg}\cdot\text{kg}^{-1}$; $155.82 \pm 12.98\text{mg}\cdot\text{kg}^{-1}$ and $265.84 \pm 33.0\text{mg}\cdot\text{kg}^{-1}$ respectively classified the soil as moderately-to-highly contaminated sandy loam soil. The contaminated soil samples were treated with various amounts (0, 2, 5, 10 and 20%) of poultry manure (pH 6.98 ± 0.50 ; organic matter $5.99 \pm 0.11\%$, cation exchange capacity $10.15 \pm 0.60\text{meq}/100\text{g}$); and sown with four viable maize grains and four viable okra seeds in each of the pots. Plants seedlings were harvested 20days after germination and analysed for their As, Cr and Cu contents by AAS. Plant uptake and accumulation levels varied in the order $\text{As} > \text{Cr} > \text{Cu}$ the order of apparent order of relative mobile fractions of the metals, and were generally higher by about an order of magnitude in maize plant than in okra plant. These results indicate the potential for the application of poultry manure in in-place immobilization of heavy metals in contaminated soil of maize plant in the phytoextraction of metals from diffusely contaminated soil.

Keywords: Phytoextraction, Heavy metals, Maize, Okra plants, Contaminated soil.

INTRODUCTION

Chromated-copper-arsenate (CCA) is one of the most widely used chemical preservative for wood against fungal attack and decay. Inadvertent spillage of the chemical, indiscriminate discharge of wood waste materials, exposure of treated wood, etc, may lead to elevated levels of As, Cr and Cu, the active components of CCA, in the vicinity of wood treatment facility. Previous studies [1-3] indicated that the land in the vicinity of an active wood treatment site in Benin City is very severely contaminated with As, Cr and Cu with potential for impacting a near-by surface water resource (Ogba River). The need to develop innovative remediation technology for the soil in the water treated site provided the impetus for this study.

Conventional cleanup technologies (*ex situ* and *in situ*) soil as soil excavation and dumping, containment methods (e.g. vitrification, stabilization), soil washing/flushing, are generally costly to be used to restore contaminated soils and are often harmful to the properties (e.g. texture and organic matter) of the soil. Phytoextraction an emerging technology which aims to remove heavy metals from contaminated soils has received much attention in recent years as environmentally friendly and cost effective method of soil remediation [4]. Initial studies focused on metal hyperaccumulating plant such as *Thalpsi*, *Urtica*, *Chenopodium*, *polygonum*, *Alyssum*, etc, but their potential application in field remediation studies is limited by the fact that they are slow growing and have small biomass yields [5]. More recent research efforts in phytoextraction have therefore shifted to crop species, which though are not metal hyperaccumulating, are quick growing and have high biomass yield [5]. The maize (*Zea mays*) and okra (*Abelmoschus esculentus*) plant fulfill these criteria and while the former has been tested in the phytoextraction of contaminated soils [6-8], reports on the latter are scanty [9].

In this study, the uptake levels of As, Cr and Cu by maize and okra plants from CCA contaminated soil amended with poultry manure are examined in pot experiments. The beneficial use of animal manure through land application is an age-long practice. In addition to their ability to favourably alter soil properties such as plant nutrient availability, organic matter content, cation exchange capacity and soil tilth [10], it is thought that livestock manure may assist in soil contaminant degradation, containment and/or plant uptake.

MATERIALS AND METHODS

Composite soil sample was collected from an active wood treatment site in Benin City. The physico-chemical properties and pollution status of the soil sample have been reported previously (Tables 1 and 2) [1-3, 8, 11]. Pre-amendment distribution of As, Cr and Cu among operationally defined pools; F₁, water soluble; F₂, exchangeable; F₃, carbonate bound; F₄, Fe-Mn oxides bound; F₅, Organic matter bound; and R, residual fractions, using the modified sequential extraction procedures proposed by Tessier *et al*, [12] are given in Table 3. Poultry manure (pH 6.60 ± 0.20; organic matter 39.50 ± 0.60%, cation exchange capacity 2.30 ± 0.80meq/100g) was applied at various levels (0-20wt%) to samples of the contaminated soil. Four viable maize grains and okra seeds were sown in each of the amended soil samples in triplicates. The plant seedlings were harvested twenty days after germination and the levels of As, Cr and Cu in the shoots determined by AAS. A detailed description of the procedure was given previously [11]. Reagent blank and analytical duplicates were used to ensure accuracy and precision of analyses. The data reported are mean values of triplicate determinations.

Tables 1: Physico-chemical properties of CCA contaminated soil

Parameters	
pH	6.20±0.40
Clay (%)	
Silt (%)	24.98±0.02
Sand (%)	2.10±0.01
Nitrogen (%)	73.10±0.06
Phosphorus (mg.kg ⁻¹)	0.34±0.08
Organic matter (%)	2.15±0.40
Cation exchange capacity (meq/100g)	47.86±0.62

Table 2: Contamination status of soil sample

Metal	Pseudototal (Σmg.kg ⁻¹)	Contamination factor, C _f	C/P index
As	32.09±2.48	91.69	1.10
Cr	265.84±33.00	757.14	10.26
Cu	155.82±12.98	16.40	1.99
C _D = degree pf contamination = ΣC _f		865.23	

$C_f = M_{contam}/M_{ref}$; M_{ref} = control soil sample; As 0.35mg.kg⁻¹; Cr 0.35mg.kg⁻¹ and Cu 9.50mg.kg⁻¹

Table 3: Geochemical forms of As, Cr and Cu in amended CCA contaminated soil

Fraction	As (mg.kg ⁻¹)	Cr (mg.kg ⁻¹)	Cu (mg.kg ⁻¹)
F ₁	4.00±0.30	13.10±0.70	1.00±0.66
F ₂	9.75±0.15	19.83±0.28	3.48±0.08
F ₃	5.00±0.10	15.10±0.50	8.80±0.20
F ₄	3.30±0.20	8.50±0.70	12.50±0.30
F ₅	2.15±0.25	38.80±0.40	26.60±0.30
R	6.85±0.35	156.18±4.03	99.30±0.40
Σ = sum of fractions	31.05±1.35	251.51±6.61	151.68±1.94
Pseudototal	32.09±2.48	265.84±3.30	155.82±2.98
Recovery (%)	96.76	94.61	97.34
Relative mobility index, M _f (%)	60.39	19.10	8.79

RESULTS AND DISCUSSION

Metal uptake by maize and okra plants:

Heavy metals uptake levels (mg.kg^{-1} dw) in maize and okra plants harvested twenty days after germination are shown in Figs 1a and 1b respectively as function of poultry manure application. The results show that levels of metal uptake decreased with increase in the level of poultry manure application. Many residuals, such as biosolids (sewage sludge) municipal solid waste compost, etc, contain sufficient amounts of organic matter, phosphates and inorganic oxides and/or have favourable properties (e.g. pH) that can reduce metal solubility and phytoavailability [13]. For example sewage sludge contains up to 50% NOM and 50% inorganic oxides of Al, Fe and Mn, silicates, phosphates and carbonates [14] which can bind/fix heavy metals. The sorbent phase responsible for the reduction of metal bioavailability in biosolids has been a subject of much interest; while some workers suggest that heavy metals are sequestered by chelation with organic matter [15], others point to the inorganic surfaces in biosolids as the heavy metals binding centers [16, 17].

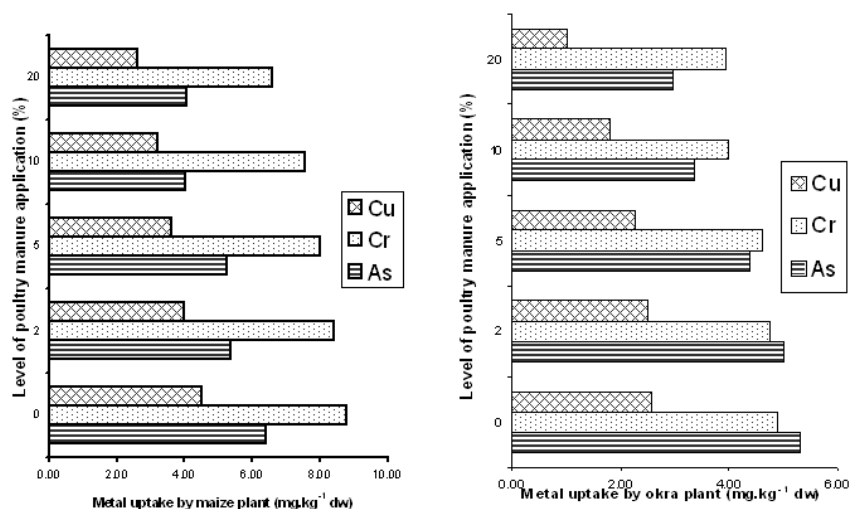


Fig. 1: Heavy metals uptake levels by (a) maize plant (b) okra plant in CCA contaminated soil amended with poultry manure

Poultry manure is rich in organic matter (about 40%) which can bind metals and make them unavailable for plant uptake. This is consistent with literature reports [18, 19] in which metal immobilization was explained in terms of organic matter-complexed and oxide-bound fractions of poultry manure. The observed decrease in metal uptake levels with increase in poultry manure loading would therefore be explained in terms of *in situ* immobilization of the metals by poultry manure. The metal pools mostly immobilized by amendment application are these relatively weakly bound to soil matrix fraction: soluble, exchangeable and carbonate-bound, converting them into unavailable (Fe-Mn oxide bound, organic matter complexed and residual) forms. Previous studies have examined the capacity of low-cost amends in reducing mobility and phytoavailability of metals in contaminated soils using chemical fractionation procedures [20, 21].

The results in Figs 1(a&b) that the amounts of metals accumulated in the maize shoots; As 4.0-6.4 mg.kg^{-1} dw; Cr 6.6-8.8 mg.kg^{-1} dw and Cu 2.6-4.50 mg.kg^{-1} dw are between 1.5-fold and 2.5-fold higher than the levels in okra plant; As 2.9 – 5.3 mg.kg^{-1} dw, Cr 3.9 – 4.9 mg.kg^{-1} dw and Cu 1.0 – 2.6 mg.kg^{-1} dw.

Plant tolerate high levels of metals in their environment using either the exclusion mechanism, by which the plant maintains metal concentrations in the shoots at constant or low levels and occurs when the entrance of metals into the roots of the plant is restricted and/or translocation of metals from the roots to the shoots of the plant is restricted [22]; or by accumulation mechanism by which metals are concentrated in plant parts [23].

High metal accumulating plant species have developed specific mechanism to detoxify the metals prior to absorption. For instance plants that tolerate high levels of arsenic are able to first through redox reaction convert the more toxic arsenic species, As^{5+} to the less toxic As^{3+} , followed by the complexation of the arsenic with phytochalinins produced by the plants [24].

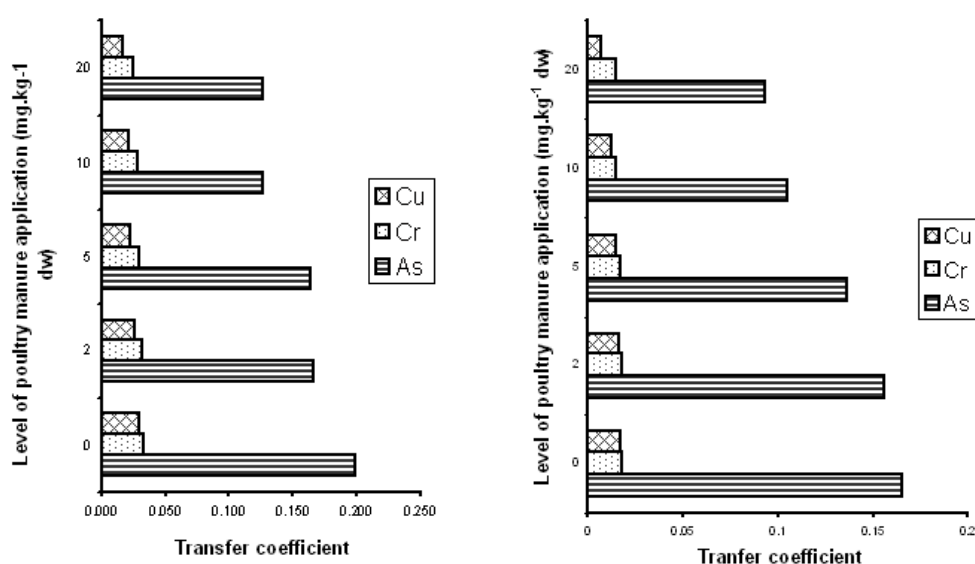


Fig 2: Transfer coefficients of As, Cr and Cu in (a) maize plant (b) okra plant in CCA contaminated soil amended with poultry maize

Metal transfer coefficient

Soil-to-plant transfer ratio is an important component of phytoextraction. Metal transfer coefficients, T_c , given as the ratio of metal concentration in plant shoots to the pseudototal concentration in the soil, obtained for As, Cr and Cu are shown in Figs 2 (a&b) for maize and okra plants respectively. These results show that the order of metal translocation is $As > Cr > Cu$ and maize plant $>$ okra plant. The transport of metals from the roots to the shoots involves long distance transfer and translocation in the xylem and storage in the vacuole of leaf cells and these processes are affected by many factors such as the concentration of available metals in soil, solubility sequences and nature of the plant species [25]. The difference in the biomass yield of maize and okra, the former being generally higher than the latter, many account in part for the observed higher levels of As, Cr and Cu accumulated in the shoots of maize plant.

CONCLUSION

This study examined the relative phytoextraction capacity of maize and okra plants for As, Cr and Cu in CCA contaminated soil amended with poultry manure. The results show that poultry manure application to contaminated soil may contribute to soil fertility and to reductions in plant available fractions of heavy metals in soil. The levels of metals uptake by maize and okra plants suggest that the plants would be suitable in phytoremediation of soils contaminated with heavy metals and that maize plant showed higher capacity than okra in the removal and accumulation of the metals.

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